

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE		3. REPORT TYPE AND DATES COVERED FINAL 30 Sep 92 TO 29 Mar 96	
4. TITLE AND SUBTITLE ORGANIC AND POLYMERIC SUPERCONDUCTORS				5. FUNDING NUMBERS F49620-92-J-0529 3484/RS 61103D	
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11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The synthetic chemistry of dithiadiazafulvalenes (DTDAF) was studied in detail: these one and two-electron donors, ore powerful than the well-known tetrathiafulvalenes (TTF, 1), but more chemically more tractable than the unstable tetraazafulvalenes, are a significant departure from ordinary organic donors, and therefore show promise in the search for new organic superconductors. A 2:5 complex of diphenyl-diacetyldithiadiazafulvalene (o2Ac2DTDAF, 4c) with the electron acceptor tetracyanoquinodimethan (TCNQ, 11a), including one molecule of acetonitrile, the solvent of crystallization (CH3CN), provided room-temperature conductivity $\sigma=0.011$ S/cm (Siemens per centimeter). An unusual diamagnetic flux exclusion signal (for 5 per cent of the sample at 4.4 Kelvin) was determined to be an artifact due to a ferromagnetic impurity. A TCNQ complex of dimethyltetracetyldTDAF, 4b had $\sigma=0.083$ S/cm at room temperature. A new acceptor, dioxotetracyanobisindanedione vinylidene (DOTCBIV), 5, provided a complex with TTF with $\sigma=0.6$ S/cm at room temperature. Many complexes wity fullerene, C60 (12), were made, but were electrically insulating. Studies of Langmuir-Blodgett films of potassium-doped C60 (monolayers on polyethylene terephthalate) may help to determine the boundary between 2-D and 3-D superconductivity.					
14. SUBJECT TERMS				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT (U)	18. SECURITY CLASSIFICATION OF THIS PAGE (U)	19. SECURITY CLASSIFICATION OF ABSTRACT (U)	20. LIMITATION OF ABSTRACT (U)		

19970314 066



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February 12, 1997

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Dear Drs. Weinstock and Lee:

Enclosed please find nine copies (sent to Dr. Lee) plus one copy (to Dr. Weinstock) of the Final Report for AFOSR Contract F-49620-92-J-0529 (Organic and Polymeric Superconductors). Thank you very much for your past support.

Robert M. Metzger
Professor

cc: Dr. Robert Wells, Assistant Vice President for Research
Pam Standifer, Contracts and Grants Accounting

Final Report to Air Force Office of Scientific Research

Date: February 12, 1997

Period 1 October 1992 - 1 March 1996

Grant Title: Organic and Polymeric Superconductors

AFOSR Grant No. F-49620-92-J-0529

Principal Investigator: Robert M. Metzger

Co-Investigator: Michael P. Cava

Institution: Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487-0336

Cognizant AFOSR Program Managers: Charles Y.C. Lee and Harold Weinstock

Abstract

The synthetic chemistry of dithiadiazafulvalenes (DTDAF) was studied in detail: these one and two-electron donors, more powerful than the well-known tetrathiafulvalenes (TTF, **1**), but more chemically more tractable than the unstable tetraazafulvalenes, are a significant departure from ordinary organic donors, and therefore show promise in the search for new organic superconductors. A 2:5 complex of diphenyldiacetyldithiadiazafulvalene ($\phi_2\text{Ac}_2\text{DTDAF}$, **4c**) with the electron acceptor tetracyanoquinodimethane (TCNQ, **11a**), including one molecule of acetonitrile, the solvent of crystallization (CH_3CN), provided room-temperature conductivity $\sigma=0.011$ S/cm (Siemens per centimeter). An unusual diamagnetic flux exclusion signal (for 5 per cent of the sample at 4.4 Kelvin) was determined to be an artifact due to a ferromagnetic impurity.

A TCNQ complex of dimethyltetracetyldTDFAF, **4b** had $\sigma=0.083$ S/cm at room temperature. A new acceptor, dioxotetracyanobisindanedione vinylidene (DOTCBIV), **5**, provided a complex with TTF with $\sigma=0.6$ S/cm at room temperature. Many complexes with fullerene, C_{60} (**12**), were made, but were electrically insulating.

Studies of Langmuir-Blodgett films of potassium-doped C_{60} (monolayers on polyethylene terephthalate) may help to determine the boundary between 2-D and 3-D superconductivity.

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1. Dithiadiazafulvalenes - New Strong Electron Donors.

As a novel variation on tetrathiafulvalene (TTF) **1**, its selenium and tellurium analogs, and their derivatives, we prepared new donors (dithiadiazafulvalenes, DTDAFs) **4a**, **4b**, **4c**, and **4d**; their electrochemistry (Table I) shows them to be powerful new donors.

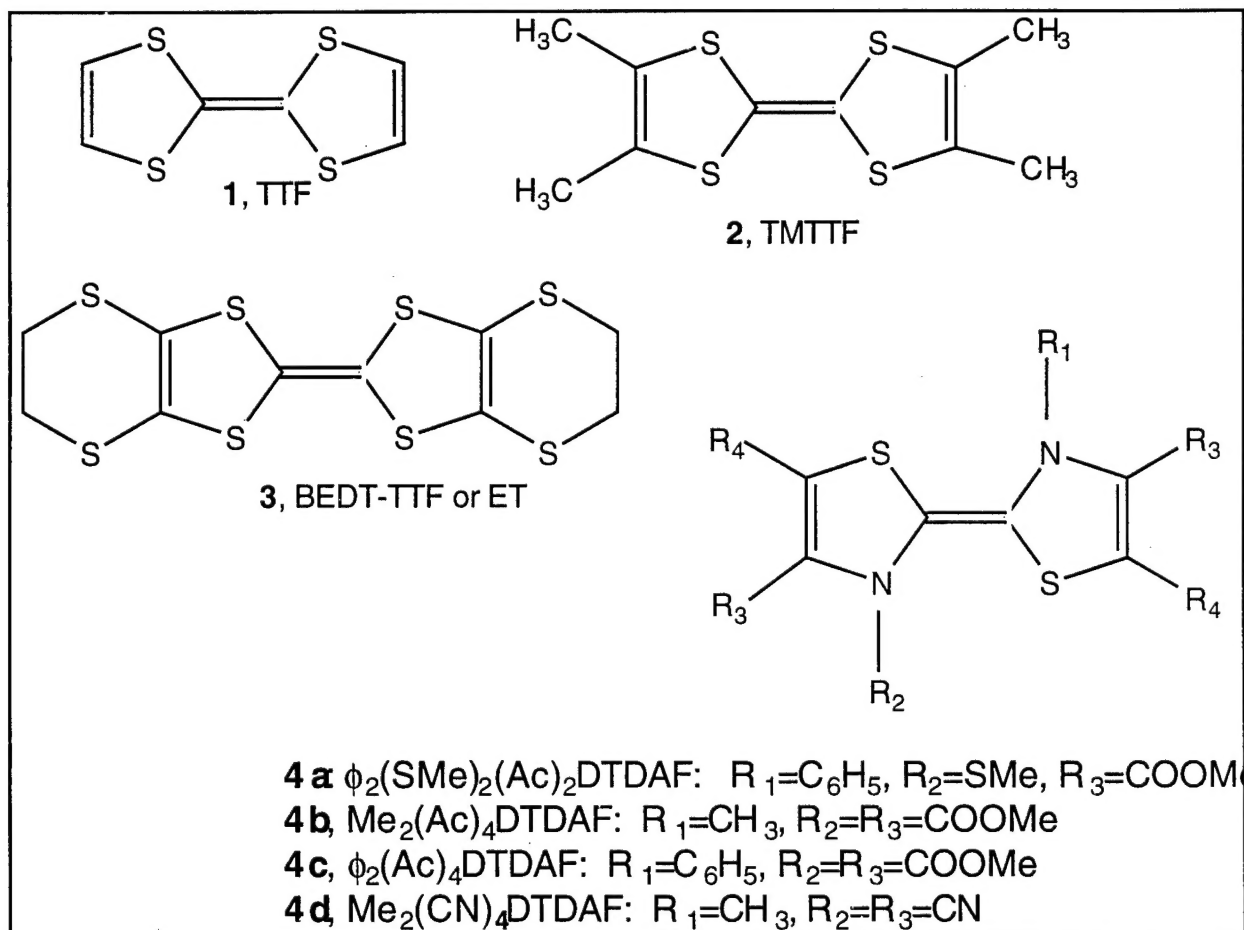


Table I. Oxidation potentials of TTF (1), TMTTF (2), and BEDT TTF (3) and of the novel DTDAFs **4a**, **4b**, **4c**, and **4d**, determined by cyclic voltammetry (V vs. SCE).

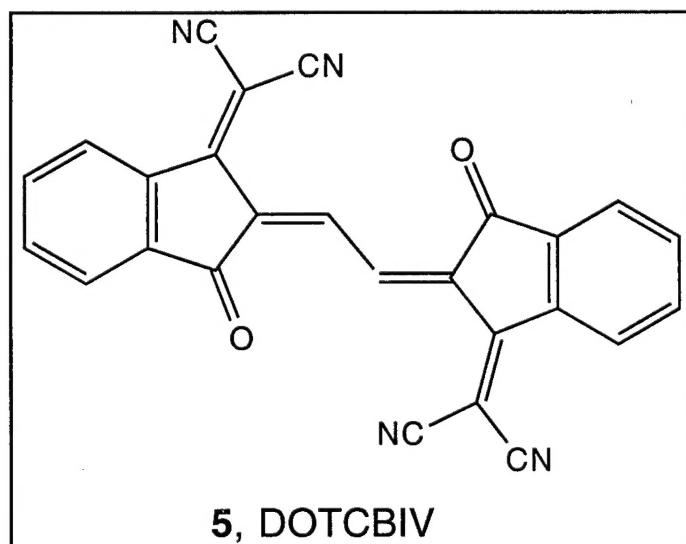
Compound	E^1_{ox} , V	E^2_{ox} , V	$E^2_{ox} - E^1_{ox}$, V
TTF (1)	0.35 [13]	0.71 [13]	0.36 [13]
TMTTF (2)	0.29 [13]	0.65 [13]	0.36 [13]
ET (3)	0.58	1.00	0.42
$\phi_2(\text{SMe})_2\text{Ac}_2\text{DTDAF}$, 4a	0.00	0.48	0.48
$\text{Me}_2\text{Ac}_4\text{DTDAF}$ 4b	0.02	0.26	0.24
$\phi_2\text{Ac}_4\text{DTDAF}$, 4c	0.15	0.66	0.51
$\text{Me}_2(\text{CN})_4\text{DTDAF}$, 4d	0.42	0.63	0.21

In complexes with the electron acceptor TCNQ, they yielded new semiconductors (Table 2) but no new metals.

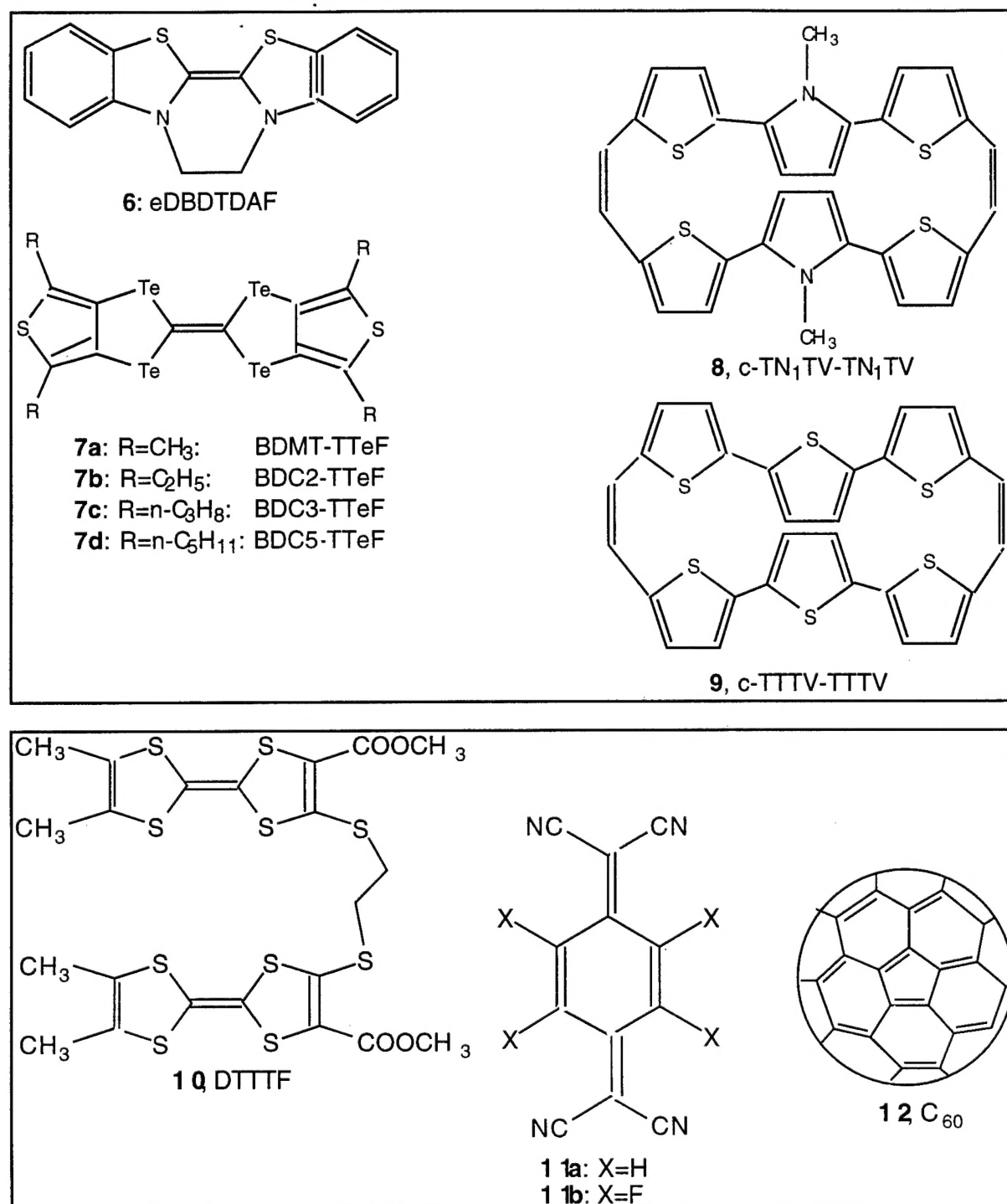
Table 2. Room temperature conductivities of complexes of **4a**, **4b**, **c** with TCNQ (standard 2-probe method, compaction, gold wire, gold paste).

Donor	Acceptor	Ratio	Conductivity (300 K) σ , S cm^{-1}
$\phi_2(\text{SMe})_2\text{Ac}_2\text{DTDAF}$, 4a	TCNQ	1:1	1.6×10^{-7}
$\phi_2(\text{SMe})_2\text{Ac}_2\text{DTDAF}$, 4a	TCNQ	1:4 (+ 2 CH_3CN)	1.1×10^{-7}
$\text{Me}_2\text{Ac}_4\text{DTDAF}$ 4b	TCNQ	1:4	8.3×10^{-2}
$\phi_2\text{Ac}_4\text{DTDAF}$, 4c	TCNQ	1:1	10^{-10}
$\phi_2\text{Ac}_4\text{DTDAF}$, 4c	TCNQ	2:5	1.1×10^{-2}

2. New Electron Acceptor



A new one-electron acceptor, dioxotetracyanobisindanedione vinylidene DOTCBIV, **5** is a strong electron acceptor, with two quasi-reversible electrochemical reduction waves ($E^1_{red} = 0.05$, $E^2_{red} = -0.11$; $E^1_{ox} = -0.06$, $E^2_{ox} = 0.11\text{V}$ vs SCE, in acetonitrile). It reacts with TTF and TMTTF to form charge-transfer complexes, whose room-temperature conductivities (2-probe method, compaction, gold wire, gold paste) are 1.7 and 0.01 S/cm respectively. An effort to prepare the octacyano derivative of BIV was not successful.



3. Physical Measurements.

The Langmuir-Blodgett films of C₆₀ [1,2] form monolayers only from very dilute dropping solutions (0.05 mg/mL), and then give areas of about 96 Å²/molecule, i.e. a true monolayer forms [3]. When doped with K, a 50 monolayer sample of C₆₀ shows a low-field signal, measured in an EPR spectrometer, with hysteresis, at or below 8.1 K: this is a sensitive test of the Meissner effect for some unknown fraction of the sample, due to the formation of K₃C₆₀ within the LB multilayer: **the world's first superconducting Langmuir-Blodgett film** [4-

6]. When more K is added, the signal disappears (formation of insulating K_6C_{60}) [4,5]. A new study of the superconductivity of K_3C_{60} LB films finds slightly higher critical temperatures [13].

The physical results for many of the complexes described in Table 3 have been published [6-9]. Overall, three are promising conductors: $(4b)_2(TCNQ)_5CH_3CN$, $4a+TCNQ$, $1+25a$. The crystal structure of the 1:5 complex of **7** with **32a** has been determined by Robert and co-workers: the neutral and anionic TCNQ species form a segregated stack, while the DTDAF cations do not overlap with each other: this is a classic "mixed" TCNQ stack structure, with expected semiconductive properties. By crystal structure analysis, $(4b)_2(TCNQ)_5CH_3CN$ forms a similar structure, with good TCNQ stacks, but where the phenyl rings on DTDAF **4b** prevent efficient stacking of the DTDAF moieties.

Table 3. List of complexes and their conductivities.

Donor	Acceptor	Solvent	Stoich.	Size, mm	Phys. Properties
$\phi_2(SMe)_2Ac_2DTDAF$, 4a	TCNQ, 11a	CH ₃ CN	1:1	powder	black $\sigma=1.6 \times 10^{-7}$ S/cm
	TCNQ, 11a	CH ₃ CN	1:4+2	CH ₃ CN	black powder $\sigma=1.12 \times 10^{-7}$ S/cm
Me ₂ Ac ₄ DTDAF, 4b	TCNQ, 11a	CH ₃ CN	1:4	powder	black powder $\sigma=8.3 \times 10^{-2}$ S/cm
ϕ_2Ac_4DTDAF , 4c	TCNQ, 11a	(CH ₂ Cl) ₂ +CH ₃ CN	2:5	1.0×0.4×0.07	black plate, $\sigma=0.011$ S/cm [9]
		CH ₂ Cl ₂	1:1	1.1×1.0×0.1	black plate, $\sigma < 10^{-10}$ S/cm [9], polycrystalline
	TCNQF ₄ , 11b	CH ₃ CN C ₆ H ₅ Cl+CH ₂ Cl ₂	1:2 1:x	small 1.6×1.1×0.01	black tiny plate black polycryst. [9] plate $\sigma=1.2 \times 10^{-6}$ S/cm
	C ₆₀ , 12	CH ₂ Cl ₂ +CS ₂	1:x	1.5×0.04×0.03	black $\sigma < 10^{-10}$ S/cm [9]
	I ₂	CHCl ₃	1:x	0.8×0.7×0.6	black $\sigma=1.1 \times 10^{-7}$ S/cm OK for X-ray [9]
		C ₂ H ₅ OC ₂ H ₅	1:x	0.5×0.04×0.04	black needle $\sigma < 10^{-10}$ S/cm [9]
eDBDTDAF, 6	TCNQ, 11a		2:1	powder	black, $\sigma < 10^{-10}$ S/cm
TTF, 1	DOTCBIV, 5	CH ₂ Cl ₂ +n-C ₆ H ₁₄	1:x	powder	$\sigma=0.6$ S/cm
BDMT-TTeF, 7a	DOTCBIV, 5	CH ₂ ClCH ₂ Cl+CS ₂	1:x	needle	black, $\sigma < 10^{-10}$ S/cm
BDMT-TTeF, 7a	TCNQ, 11a	CH ₂ ClCH ₂ Cl	1:x		tiny plate
	C ₆₀ , 12	CS ₂	1:x		tiny plate.
		CS ₂	1:1+1	CS ₂	rhombic plate, cryst.str. [6] $\sigma < 10^{-10}$ S/cm [7]
BD2T-TTeF, 7b	C ₆₀ , 12	CS ₂ CH ₂ Cl ₂ +CS ₂	1:x 1:x	 1.0×0.9×0.04	hexagonal plate black polycrystal, $\sigma < 10^{-10}$ S/cm
BD3T-TTeF, 7c	C ₆₀ , 12	CS ₂	1:x	0.8×0.7×0.02	$\sigma < 10^{-10}$ S/cm
BD5T-TTeF, 7d	C ₆₀ , 12	CS ₂	1:x	0.4×0.3×0.02	$\sigma < 10^{-10}$ S/cm
DTTF, 10	C ₆₀ , 12	CS ₂ or C ₆ H ₆	1:x	1.5×0.05×0.04	needle, insulator [9]
c-TTTV-TTTV, 8	TCNQF ₄ , 11b		1:1	powder	$\sigma=9.5 \times 10^{-3}$ S/cm [8]
c-TN ₁ TV-TN ₁ TV, 9	TCNQF ₄ , 11b		1:1	powder	$\sigma=1.2 \times 10^{-4}$ S/cm [8]

The synthetic chemistry of the dithiadiazafulvalenes has been published in full [10]. The criteria for the formation of organic superconductors, and of the limiting conductivity of organic polymers has been published [11]. A new polymeric semiconductor has also been studied [12].

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5. Personnel supported by this contract

Dr. Ping Wang (present employment: Samsung Industries, San Jose, CA)

Dr. Gregory V. Tormos (present employment: Eastman Chemical Co., Batesville, AR)

6. Patents and inventions supported by this contract.

None.